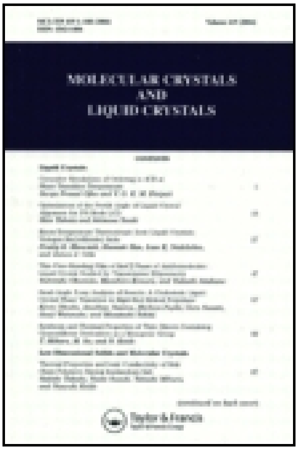

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# Transient Absorption Spectroscopy for Photochemical Reactions of a Negative Photochromic Spiropyran

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# Transient Absorption Spectroscopy for Photochemical Reactions of a Negative Photochromic Spiropyran

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We have measured the transient absorption of a negative photochromic spiropyran derivative, 3′,3′-dimethyl-6,8-dinitro-1′-octadecylspiro[(2H)-1-benzopyran-2′,2-indoline] by a nanosecond laser photolysis, in order to elucidate the dynamical behavior of the negative photochromic reactions. On visible light photolysis, the intensity of the absorption bands of the merocyanine (MC) form decreases and that of the spiropyran (SP) form increases. The transient absorption of the MC form consists of three bleaching components with the time constants of ≤25 ns, 240 ns and 3.4 μs. On the other hand, the transient absorption of the SP form has two rising components with the time constants of 620 ns and 4.0 μs. Based on the analogy to the photochromic reaction of the positive photochromic spiropyrans, the reaction pathway from the MC to SP form of the negative photochromic spiropyrans is discussed.

*Keywords:* negative photochromism; spiropyran; nanosecond laser photolysis

## INTRODUCTION

The photochromic properties of spiropyrans have been studied intensively not only for practical applications but also for fundamental interest of photochemistry.

Recently, negative photochromic spiropyran derivatives have been synthesized, because they are potentially promising candidates for new functional photodevices [1,2]. However, as far as we know, no dynamical behavior of the negative photochromic reaction has been reported so far. In order to elucidate the dynamical behavior of the negative photochromic reaction, we have measured the transient absorption change of a negative photochromic spiropyran derivative, 3',3'-dimethyl-6,8-dinitro-1'-octadecylspiro[(2H)-1-benzopyran-2',2'-indoline] (**1**) by a nanosecond laser photolysis for the first time.

Figure 1 shows the molecular structure as well as the chemical reactions of the compound **1**. The compound **1** has two basic forms: an intensely colored merocyanine (MC) form and a colorless spiropyran (SP) form. The MC form is thermally stable relative to the SP form due to the existence of two nitro groups and a relatively long $R_1$ structure. The MC form changes to the SP form on irradiation of visible light and the SP form returns back to the MC form by UV irradiation or heating.

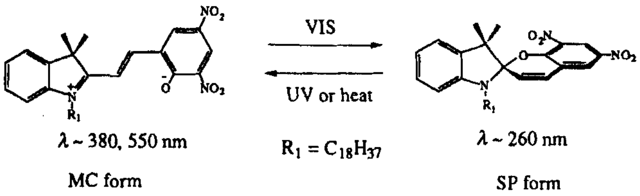

FIGURE 1 Molecular structure and chemical reactions of a negative photochromic spiropyran **1**.

## EXPERIMENTAL

The compound **1** was dissolved into 1,2-dichloroethane with a concentration of 2 x $10^{-4}$ M (mol/dm$^3$). During the laser photolysis measurement, the solution of the compound **1** was circulated by a peristaltic pump through a flow cell with a 2 mm thickness. The sample was deoxygenated by bubbling with nitrogen during the experiment.

The second harmonic (532 nm) of an Nd:YAG laser with a pulse duration of 3 ns was used as an excitation laser source for the transient absorption measurement. The excitation wavelength lies at the lowest absorption band of the MC form. Tungsten and deuterium lamps were used as a probing light source. The probe and excitation beams were impinged upon the same position of the sample. The probe beam after passing through the sample was focused onto an entrance slit of a single monochromator and detected by a photomaltiplier and a digital sampling oscilloscope. The timing between the laser and the oscilloscope was synchronized by a digital delay generator. The overall time resolution of the system was about 25 ns. The transient absorption change ($\Delta$ OD) was measured in a spectral region of 250-500 nm. Due to a strong fluorescence from the MC form, we could not measure the transient $\Delta$ OD in a visible light region above 500 nm.

## RESULTS AND DISCUSSION

Figure 2 shows the ordinary absorption spectra of the compound **1** for various visible light irradiation times. The absorption change is also shown in the figure. On visible light irradiation, the intensity of the absorption bands due to the MC form (550, 380 nm) decreases and that of the SP form (260 nm) increases with increasing the irradiation time as shown by solid arrows. The existence of the isosbestic point at 290 nm suggests that the photochromic reaction of the compound **1** takes place between the two forms, the MC and SP forms, in steady state. We also found a strong fluorescence from the MC form which lies in the visible light region of 550-700 nm.

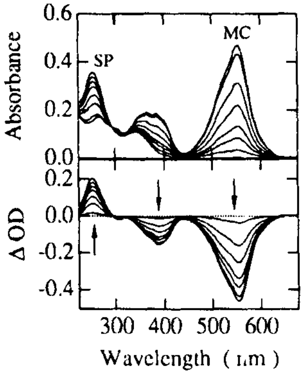

FIGURE 2 Absorption spectra of the compound **1** for different visible light irradiation times, 0, 1, 5, 10, 20, 30, 120 and 600 min. The $\Delta$ OD spectra are also depicted in the figure.

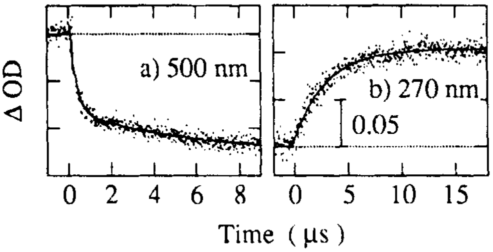

FIGURE 3 Time evolution of the transient absorption change for the MC (a) and SP (b) forms of the compound **1**.

Typical time evolution of the transient absorption change for the MC and SP forms of the compound **1** is shown in Figs. 3a) and 3b). The probe wavelengths are 500 and 270 nm, respectively. The transient absorption of the MC form consists of three bleaching components. The first component bleaches in time less than the time resolution of the instrumental response (≤25 ns), while the slower components bleach with the time constants of 240 ns and 3.4 μs, respectively. On the other hand, the transient absorption of the SP form consists of two rising components with the time constants of 620 and 4.0 μs. These time constants are almost independent of the probe wavelength for the MC or SP form. The slowest bleaching time of the MC form (3.4 μs) is almost equal to the slower rise time of the SP form (4.0 μs). On the other hand, the time constant of the fast components is quite different between the MC and SP forms. Especially, no fast rise within the time resolution of the instrumental response was observed for the SP form. This suggests that an intermediate conformation should exist on the reaction pathway from the MC to SP form.

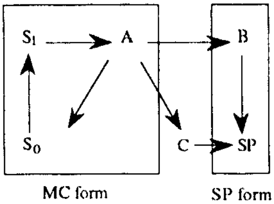

FIGURE 4 Proposed model of the negative photochromic reaction of the compound **1**.

It is well known that the photomerocyanine form is formed both via singlet and triplet states of the open form for the positive photochromic spiropyrans having a nitro group [3,4].

Based on the analogy to the photochromic reaction of the positive photochromic spiropyrans [3,4], we tentatively propose a model of the reaction pathway for the negative photochromic reaction of the compound **1**, where we take into account the triplet states of both the MC and SP forms. The model is schematically shown in Fig. 4. On visible light photolysis, the self-bleaching of the absorption of the singlet state and the internal conversion from the singlet ($S_1$) to lowest triplet state (A) of the MC form occur within the time resolution of the instrumental response (≤25 ns). Next, the conversions from the A to the triplet state of the SP form (B) and to the ground state of the intermediate open form (C) take place with the time constant of 240 ns. Finally, the B and C convert to the ground state of the SP form (SP) with the time constants of 620 ns and 3-4 μs, respectively.

The transient absorption of the triplet state was observed at ~700 nm on the positive photochromic spiropyrans [3]. To find the triplet states of the MC and SP forms of the compound **1**, the transient absorption experiment in the visible light region of 550-700 nm is now in progress.

## CONCLUSION

We have measured the transient absorption of a negative photochromic spiropyran derivative, 3',3'-dimethyl-6,8-dinitro-1'-octadecylspiro[(2H)-1-benzopyran-2',2'-indoline] by the nanosecond laser photolysis, in order to elucidate the dynamical behavior of the negative photochromic reactions. On visible light photolysis, the intensity of the absorption bands due to the MC form decreases and that of the SP form increases. The transient absorption of the MC form consists of three bleaching components with the time constants of ≤25 ns, 240 ns and 3.4 μs. On the other hand, the transient absorption of the SP form has two rising components with the time constants of 620 ns and 4.0 μs. Based on the analogy to the photochromic reaction of the positive photochromic spiropyrans, we propose a model of the reaction pathway from the MC to SP form of the negative photochromic spiropyrans for the first time.

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